

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number
WO 2004/024788 A1

(51) International Patent Classification⁷: **C08F 214/18**,
214/22, C08K 3/00, 5/14, 5/00

(21) International Application Number:
PCT/US2003/028472

(22) International Filing Date:
11 September 2003 (11.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/410,138 12 September 2002 (12.09.2002) US

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: **FUKUSHI, Tatsuo**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **WORM, Allan T.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **HARE, Erik D.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **BENNETT, Gregory S.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **COGGIO, William D.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **SZYMANSKI, Brian E.**, et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **FLUROELASTOMERS WITH IMPROVED PERMEATION RESISTANCE AND METHOD FOR MAKING THE SAME**

(57) Abstract: A compound is prepared, suitable for forming fluoroelastomers, having the unique features of a low glass transition temperature and desirable permeation resistance. The compound generally comprises two primary components. The first component is an amorphous copolymer including interpolymerized units derived from one or more perfluorinated ethers. The second component is a curable component including at least one filler having at least 10 parts per 100 parts of the first component. Upon vulcanization the resulting elastomeric compound has desirable physical characteristics as indicated by the durometer, the retraction at lower temperatures (TR-10) and permeation resistance.

WO 2004/024788 A1

FLUOROELASTOMERS WITH IMPROVED PERMEATION RESISTANCE AND METHOD FOR MAKING THE SAME

Field of the Invention

5 The present invention relates to a compound suitable for forming a fluoroelastomer having distinguished low temperature characteristics and improved permeation resistance. The present invention also includes a process for producing the fluoroelastomer.

Background of the Invention

10 Increasingly stringent evaporative fuel standards for automobiles and trucks demand that the fuel system component minimize the emission of fuel vapors through automotive components such as the fuel tank, fuel filler lines, fuel injector seals, and fuel seals. Elastomers employed in fuel seal applications generally require low temperature properties, *e.g.* glass transition temperature (T_g) $< -20^\circ\text{C}$ to maintain sealing performance for cold weather. Various types of fluoroelastomers for fuel seals have been proposed to address these concerns. In
15 general, the most successful of the elastomers generally contain perfluoromethylvinylether (PMVE). PMVE reduces the glass transition temperature but generally has an adverse effect upon permeation. Materials with the combination of improved low temperature sealing and better permeation resistant materials are needed to meet the regulations, which has consistently been moving toward zero fuel emission.

20 Because of the expense of the fluoroelastomer, especially PMVE monomer, it is often desirable to use an extender compounded with the fluoroelastomer. However, compared to other hydrocarbon elastomers, fluoroelastomer combined with a low loading filler provides an unusually high durometer. Thus rendering the compound ineffective for sealing applications.

25 Those skilled in the art of fluoroelastomers recognize that it is difficult to get low temperature performance while maintaining good permeation resistance. It would be an advantage to improve the fuel permeation rate of an elastomer while retaining low temperature performance.

Summary of the Invention

30 The present invention is directed to a compound suitable for forming fluoroelastomers having the unique features of a low glass transition temperature and desirable permeation resistance. The compound generally comprises two main components. The first component is

an amorphous copolymer including interpolymerized units derived from one or more perfluorinated ethers of the formula:

$\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f$ (Formula I) wherein R_f is a perfluorinated (C1-C 4)alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$, or

5 $\text{CF}_2=\text{CF}(\text{CF}_2)_m-\text{O}-\text{R}_f$ (Formula II) wherein: $m=1-4$; R_f is a perfluorinated aliphatic group optionally containing O atoms.

The second component is a curable component including at least one filler having at least 10 parts per 100 parts of the first component. Upon vulcanization the resulting elastomeric compound has desirable physical characteristics as indicated by the durometer, the retraction at 10 lower temperatures (TR-10) and the permeation resistance.

With respect to the durometer the present invention generally exhibits a Shore A hardness according to ASTM D2240-02 of 60 or greater and preferably 65-85.

The retraction at lower temperatures (TR-10) according to ASTM D 1329-88 is of -25°C or less and preferably -30°C or less.

15 The elastomeric compound also has a permeation rate (CE10) of 65 (g-mm/m²-day) or less and preferably 60 (g-mm/m²-day) or less. The noted physical characteristics make the fluoroelastomer well suited for sealing applications.

The compound of the present invention may generally include various copolymers terpolymers or quadpolymers in conjunction with the perfluorinated ethers. The preferred 20 embodiment utilizes vinylidene fluoride to achieve the beneficial physical characteristics while achieving desirable economics.

The compound of the present invention may be vulcanized using conventional methods. Further, the articles produced using the present compound are suitable for various sealing applications, including applications in the automotive industry.

25

Detailed Description

The present invention is directed to a polymeric compound that is suitable for use, upon vulcanization, as a fluoroelastomer for sealing applications. The polymeric compound is generally a two component system comprising an amorphous copolymer that includes specific 30 perfluorinated ethers. The second component is a curable component that includes at least one filler. The compound may include one or more conventional adjuvants, such as, for example, crosslinking agents such as peroxides, coagents, and acid acceptors. The perfluorinated ethers of the present invention assist in achieving the desired glass transition temperature and the fillers

are directed to reducing the permeation rate of the resulting vulcanized article. For purposes of the present invention, an amorphous copolymer is one that has essentially no detectable melting endotherm or crystalline exotherm peak, as determined by differential scanning calorimetry (DSC).

5 The first component of the present invention is generally a copolymer that includes interpolymerized units of at least one perfluorinated ether and interpolymerized units of another conventional monomer. For purposes of the present invention, the term copolymer is intended to include a polymer derived from two or more monomeric units. In preferred embodiments, the present invention may include specific terpolymers or quadpolymers that are employed to
10 achieve specific physical characteristics in the final vulcanized compound.

Non-limiting examples of suitable monomers include compositions selected from vinylidene fluoride, tetrafluoroethylene, hexafluoro propylene, vinyl ethers, chloro trifluoro ethylene, pentafluoropropylene, vinyl fluoride, propylene, and ethylene. Combinations of the noted monomers may also be employed in the first component of the present invention. The
15 first component may also include ethylenically unsaturated monomers of the formula $\text{CF}_2=\text{CFR}_f$ where R_f is fluorine or perfluoroalkyl of 1 to 8 carbon atoms.

Those skilled in the art are capable of selecting specific monomers at appropriate amounts to form an elastomeric polymer. Thus the appropriate level of monomers, based on mole %, are selected to achieve an amorphous polymeric composition.

20 Preferably, the fluorocarbon polymers of the present invention include about 50-80 mole% of the repeating units derived from vinylidene fluoride (VF_2), and about 10-50 mole% of the repeating units derived from the perfluorinated ether of Formula I, with or without a halogen cure site. They can optionally include up to about 40 mole% of repeating units derived from a fluoromonoolefin other than the perfluorinated ether and vinylidene fluoride. Such other
25 fluoromonoolefins include, for example, tetrafluoroethylene (TFE), hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE), 1-hydropentafluoropropene, perfluoro(methylvinylether) perfluoro(propylvinylether), perfluorocyclobutene, and perfluoro(methylcyclopropene). Optionally, the aforementioned one or more fluoromonoolefins may be copolymerized with fluorine-free olefinic monomers such as ethylene and propylene.

30 In a preferred embodiment, the present invention is a quadpolymer generated from tetrafluoroethylene, vinylidene fluoride, a perfluorinated vinyl ether of the formula $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, and a perfluoroalkyl vinylether of the formula $\text{CF}_2=\text{CFO}(\text{CF}_2)_m\text{CF}_3$ wherein: $m=0-4$, and preferably perfluoromethyl vinylether. This specific embodiment

exhibits desirable solvent swell and glass transition temperatures that are very desirable for sealing applications. The quadpolymer composition is fully detailed in U.S. Patent Application _____ filed on September ___, 2003 (Attorney Docket No. 58041US004), herein incorporated by reference in its entirety.

5 In an alternative preferred embodiment, the fluorocarbon polymers of the present invention include about 40-65 mole% of the repeating units derived from vinylidene fluoride (VF₂), and about 10-50 mole-% of the repeating units derived from the perfluorinated ether of Formula I, and about 1-15 mole-% of the repeating units derived from the perfluoromethyl vinyl ether of Formula II with or without a halogen cure site. They can optionally include up to
10 about 40 mole% of repeating units derived from a fluoroolefin other than the perfluorinated ether and vinylidene fluoride. Such other fluoromonoolefins include, for example, hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), 1-hydropentafluoropropene, perfluorocyclobutene, and perfluoro(methylcyclopropene). Optionally, the aforementioned one or more fluoromonoolefins may be copolymerized with
15 fluorine-free olefinic monomers such as ethylene and propylene.

One or more perfluorinated ethers are employed in the compound. The perfluorinated ethers have the formula of:

$\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f$ (Formula I) wherein R_f is a perfluorinated (C1 -C4) alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$, or

20 $\text{CF}_2=\text{CF}(\text{CF}_2)_m-\text{O}-\text{R}_f$ (Formula II) wherein: $m=1-4$; R_f is a perfluorinated aliphatic group optionally containing O atoms.

The perfluorinated ethers are included in amounts that enable the formation of an amorphous compound. Those skilled in the art are capable of selecting an appropriate mole%, in combination with at least one other monomer, to achieve the desired properties.

25 The perfluorinated ether components result in a compound that is capable of retaining a preferred elasticity, as indicated by a Shore A hardness value, while retaining a desired retraction at lower temperature (TR-10). The retention of the flexibility and retraction at lower temperature (TR-10) enable the use of fillers in the compound at levels that enhance the permeation resistance of the vulcanized compound.

30 The most preferred perfluorinated ethers are selected from:

$\text{CF}_2=\text{CFOCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$

$\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2(\text{OCF}_2)_3\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2(\text{OCF}_2)_4\text{OCF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$
5 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$, and
 $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{OCF}_3$.

Additionally, combinations of the noted perfluorinated ethers may be used.

10 A component of the amorphous copolymer may generally includes an effective amount
 of cure site moieties derived from one or more compounds of the formula: a) $\text{CX}_2=\text{CX}(\text{Z})$,
 wherein: (i) X is H or F; and (ii) Z is Br, I, Cl or R_2U wherein U=Br, I, Cl, or CN and R_2 =a
 perfluorinated divalent linking group optionally containing O atoms; or (b) $\text{Y}(\text{CF}_2)_q\text{Y}$,
 wherein: (i) Y is Br or I or Cl and (ii) $q=1-6$. Preferably the cure site moieties are derived from
 15 one or more compounds selected from the group consisting of $\text{CF}_2=\text{CFBr}$, $\text{CF}_2=\text{CHBr}$, ICF_2
 $\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, CH_2I_2 , $\text{BrCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFO}(\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{Br}$, CH_2
 $=\text{CHCF}_2\text{CF}_2\text{Br}$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{I}$, $\text{CF}_2=\text{CFCl}$ or mixtures thereof. In a most preferred
 embodiment, the iodine, bromine, or chlorine are chemically bound to chain ends of the first
 component of the compound. Optionally, nitrile cure site moieties may also be utilized. The
 20 crosslinkable composition can further include one or more substances known to promote the
 formation of triazine rings by trimerization of nitriles under the influence of heat. These include
 organometallic compounds of arsenic, antimony, and tin described in U.S. Pat. Nos. 3,470,176,
 3,546,186, and the metal oxides described in U.S. Pat. No. 3,523,118, all herein incorporated by
 reference in their entirety.

25 The compound also includes a curable component that enables vulcanization of the
 fluoropolymer. The curable component may include curable materials, such as, for example,
 peroxide or one or more co-agents. Peroxide curatives include organic or inorganic peroxides.
 Organic peroxides are preferred, particularly those that do not decompose during dynamic
 mixing temperatures. Examples of non-limiting peroxides include dicumyl peroxide, 2,5-
 30 dimethyl-2,5-di(tbutylperoxy)hexane, di-t-butyl peroxide, t-butylperoxy benzoate, 2,5-dimethyl-
 2,5-di(t-butylperoxy)hexane-3 and laurel peroxide. Other suitable peroxide curatives are listed
 in U.S. Pat. No. 5,225,504 (Tatsu et al.). The amount of peroxide curing agent used generally

will be 0.1 to 5, preferably 1 to 3 parts per 100 parts of fluoropolymer. Other conventional radical initiator are suitable for use with the present invention.

In peroxide vulcanization of the fluorocarbon polymer using an organic peroxide, it is often desirable to include a co-agent. Those skilled in the art are capable of selecting
5 conventional co-agents based on desired physical properties. Non-limiting examples of such agents include tri(methyl)allyl isocyanurate (TMAIC), triallyl isocyanurate (TAIC), tri(methyl)allyl cyanurate, poly-triallyl isocyanurate (poly-TAIC), xylylene-bis(diallyl isocyanurate) (XBD), N,N'-m-phenylene bismaleimide, diallyl phthalate, tris(diallylamine)-s-triazine, triallyl phosphite, 1,2-polybutadiene, ethyleneglycol diacrylate, diethyleneglycol
10 diacrylate, etc. Another useful co-agent may be represented by the formula $\text{CH}_2=\text{CH}-\text{R}_f^1-\text{CH}=\text{CH}_2$ wherein R_f^1 is as described above. Such co-agents provide enhanced mechanical strength to the final cured elastomer. They generally are used in amount of 1 to 10 parts, or preferably 1 to 5 parts, per 100 parts of the fluorocarbon polymer.

The curable component also includes fillers that may improve the permeation rate of the
15 compound. The fillers are included at about at least 10 parts per 100 parts of the first component of the compound. Non-limiting examples of fillers include carbon black, graphite, conventionally recognized thermoplastic fluoropolymer micropowders, clay, silica, talc, diatomaceous earth, barium sulfate, wollastonite, calcium carbonate, calcium fluoride, titanium oxide, and iron oxide. Combinations of conventional fillers may also be employed. Those
20 skilled in the art are capable of selecting specific fillers at amounts in the noted range to achieve desired physical characteristics in the vulcanized compound.

Conventional adjuvants may also be incorporated into the compound of the present invention to enhance the properties of the compound. For example, acid acceptors may be employed to facilitate the cure and thermal stability of the compound. Suitable acid acceptors
25 may include magnesium oxide, lead oxide, calcium oxide, calcium hydroxide, dibasic lead phosphite, zinc oxide, barium carbonate, strontium hydroxide, calcium carbonate, hydrotalcite, alkali stearates, magnesium oxalate, or combinations thereof. The acid acceptors are used in amounts ranging from about 1 to about 25 parts per 100 parts by weight of the polymer.

The polymers of this invention may be prepared using free radical batch or semi-batch,
30 or continuous free radical emulsion polymerization processes. They may also be prepared by free radical suspension polymerization processes.

For example, if a continuous emulsion process is utilized, the polymers are generally prepared in a continuous stirred tank reactor. Polymerization temperatures may be in the range

of 40° to 145°C, preferably 100° to 135°C. at pressures of 2 to 8 MPa. Residence times of 20 to 60 minutes are preferred. Free radical generation may be effected through use of a water-soluble initiator such as ammonium persulfate, either by thermal decomposition or by reaction with a reducing agent such as sodium sulfite. An inert surface-active agent such as ammonium perfluorooctanoate may be utilized to stabilize the dispersion, usually in conjunction with addition of a base such as sodium hydroxide or a buffer such as disodium phosphate to control pH in the range 3 to 7. Unreacted monomer is removed from the reactor effluent latex by vaporization at reduced pressure. Polymer is recovered from the stripped latex by coagulation. For example, coagulation may be effected by reducing latex pH to about 3 by addition of acid, then adding a salt solution, such as an aqueous solution of calcium nitrate, magnesium sulfate, or potassium aluminum sulfate, to the acidified latex. The polymer is separated from the serum, then washed with water and subsequently dried. After drying, the product may be cured.

Chain transfer agents may be used in the polymerization in order to control the molecular weight distribution of the resulting polymers. Examples of chain transfer agents include isopropanol; methyl ethyl ketone; ethyl acetate; diethyl malonate; isopentane; 1,3-diiodoperfluoropropane; 1,4-diiodoperfluorobutane; 1,6-diiodoperfluorohexane; 1,8-diiodoperfluorooctane; methylene iodide; trifluoromethyl iodide; perfluoro(isopropyl) iodide; and perfluoro(n-heptyl) iodide. Polymerization in the presence of iodine-containing chain transfer agents may result in a polymer with one or two iodine atoms per fluoroelastomer polymer chain, bound at the chain ends (see for example U. S. Pat. No. 4,243,770 and U.S. Pat. No. 4,361,678, herein incorporated by reference in their entirety). Such polymers may have improved flow and processability compared to polymers made in the absence of a chain transfer agent. Generally, up to about 1 weight percent iodine chemically bound to fluoroelastomer chain ends will be incorporated into the polymer, preferably from 0.1-0.3 wt. %.

The crosslinkable fluoropolymer composition can be compounded with the curable component or mixed in one or several steps, using any of the usual rubber mixing devices such as internal mixers (e.g., Banbury mixers), roll mills, etc. For best results, the temperature of the mixture should not rise above about 120°C. During mixing it is necessary to distribute the components and additives uniformly throughout for effective cure.

The mixture is then processed and shaped, for example, by extrusion (for example in the shape of a hose or hose lining) or molding (for example, in the form of an O-ring seal). The shaped article can then be heated to cure the gum composition and form a cured elastomer article.

Pressing of the compounded mixture (i.e., press cure) is typically conducted at a temperature of about 95-230°C, preferably about 150-205°C, for a period of about 1 minute to about 15 hours, usually for about 1-10 minutes. A pressure of about 700-20,000 kPa, preferably about 3400- 6800 kPa, is typically used in molding the composition. The molds first may be coated with a release agent and prebaked.

The molded vulcanizate is then usually post cured in an oven at a temperature of about 150-315°C, preferably at a temperature of about 200-260°C, for a period of about 2-50 hours or more, depending on the cross-sectional thickness of the sample. For thick sections, the temperature during the post cure is usually raised gradually from the lower limit of the range to the desired maximum temperature. The maximum temperature used is preferably about 260°C, and is held at this value for about 4 hours or more.

The cured compound of the present invention exhibits a combination of beneficial physical characteristics relating to durometer, retraction at lower temperature (TR-10 and permeation rate when compared to conventional compounds. The compound exhibits a low durometer value, as indicated by the Shore A hardness test (ASTM D2240-02) of about 60 or greater, and preferably 65-85. The durometer value is an indication of the elasticity and viscoelastic behavior of the material. The compound also has a TR-10 of about -25°C or less, and preferably -30°C or less. The CE10 fuel permeation rate of the compound at 40°C, as measured using a modified version of the procedure described in ASTM D 814-95 (Reapproved 2000), as set forth in the Examples section below, is 65 (g-mm/m²-day) or less, preferably 60 (g-mm/m²-day) or less, most preferably about 55 (g-mm/m²-day) or less. The resulting compound exhibits a solvent volume swell in Fuel K (CM85) for 70 hours at 40°C of about 60% or less, according to ASTM D471-98. The combination of the noted physical characteristics make the curable compound well suited for sealing applications that require low temperature performance with excellent permeation resistance.

The invention is further illustrated in the following examples.

Examples

In the following Examples and Comparative Examples all concentrations and percentages are by weight unless otherwise indicated. The fluoroelastomer gums were prepared according to the method described in US Pat. No. 6,294,627, which is incorporated by reference in its entirety. The monomer composition ratios of the fluoroelastomers used in the Examples are shown in Table 1. The fluoroelastomer compounds, which are used in the Examples and

Comparative Examples, also are summarized in Table 1. Table 2 summarizes the physical properties for Examples 1-5 and Comparative Examples 1-4. Unless otherwise noted, all amounts in Table 2 are expressed in parts by weight, or parts by weight per one hundred parts by weight of rubber (phr). As represented in the Tables, VDF is vinylidene fluoride, TFE is tetrafluoroethylene, PMVE is perfluoromethylvinylether, MV-31 is perfluoro-3-methoxypropyl vinyl ether ($\text{CF}_2=\text{CFO}(\text{CF}_2)_3\text{OCF}_3$), and CSM is cure site monomer.

Fluoropolymers

The fluoropolymers listed in Table 1 were used in this invention. The monomer composition ratio was determined by ^{19}F -NMR. The Mooney viscosity of the materials was determined by ASTM 1646-00 (ML 1+10@ 121°C). Results are reported in Mooney units. The glass transition points (T_g) were obtained from the midpoint temperature of the peak at a temperature rate of 20°C/min. No melting peak or point was detected for each polymer sample by differential scanning calorimetry (DSC) scan from 0 to 200°C.

Table 1

Fluoro-elastomer	Monomer composition ratio (mol%)					DSC scan (-60 to 200°C)		Mooney viscosity (ML 1+10 @121°C)
	VDF	TFE	MV-31	PMVE	CSM	T_g (°C)	melt peak	
LTFE 1	57.9	21	20.9	0	0.2	-41	N/D	110
LTFE 2	59	20	9.3	11	0.7	-32	N/D	70
GLT305	77	5	0	18	a CSM	-31	N/D	32

N/D: not detected.

Test Methods

Mooney viscosity was determined by ASTM 1646-00 (ML 1+10@ 121°C). Results are reported in Mooney units.

Cure Rheology Tests were run on uncured, compounded admixtures using an Alpha Technology Moving Disk Rheometer (MDR) Model 2000 in accordance with ASTM D 5289-95 at 177°C, no preheat, 12 minute elapsed time (unless otherwise specified) and a 0.5°C. arc. Minimum torque (M L), Maximum torque (M H), i.e., highest torque attained during specified period of time when no plateau or maximum was obtained and Difference in Torque, ΔT , i.e., (M H - M L),

were reported. Also reported were: t_2 (time for torque to increase 2 units above M_L), t'_{50} (time for torque to reach $M_L + 0.5[M_H - M_L]$), and t'_{90} (time for torque to reach $M_L + 0.9[M_H - M_L]$).

- 5 **Press-cured samples** (150×75×2.0 mm sheets, unless otherwise noted) were prepared for physical property determination by pressing at about 6.9×10^3 kPa for 10 minutes at 177°C.

Post cure samples were prepared by placing a press-cured sample in a circulating air oven. The oven was maintained at 230°C and the samples treated for 16 hours.

- 10 **Tensile Strength at Break, Elongation at Break, and Modulus at 100% Elongation** were determined using ASTM D 412-98 on samples cut from 2.0 mm sheet with ASTM Die D. Units are reported in Mega Pascals (MPa).

Durometer or hardness was determined using ASTM D 2240-02 Method A with a Type A-2 Shore Durometer. Units are reported in points.

Retraction at Lower Temperatures (TR-10) was determined using ASTM D 1329-88 (reapproved 1998) with ethanol as the cooling media. Units are reported in °C.

- 15 **Solvent Volume swell** was determined with according to ASTM D 471-98 Method using Fuel K (CM85; 85% methanol, 7.5% iso-octane; 7.5% toluene by volume) at 40°C for 70 hours.

Compression set (C/set) was determined by ASTM D 395-01 Method B with 0.139 inch (3.5 mm) O-rings compressed for 70 hours at 200°C. Results are reported as percentages.

- 20 **Glass transition temperature (T_g) and detection of melting peak or point (T_m , an endothermic process)** was determined in accordance with ASTM D 793-01 and ASTM E 1356-98 by a Perkin-Elmer differential scanning calorimetry DSC 7.0 at under a nitrogen flow and a heating rate of 20°C/min. DSC scan was obtained from -40°C to 200°C at 20°C/min. scan rate.

- 25 **Fuel permeation constant** was determined by the following method. A post cured sheet (press cure: 10 minutes at 177°C, post cure: 16 hours at 230°C) was cut into a disc having a diameter of 7.72 cm and used for permeation testing. Permeation constants were obtained using the procedure described in ASTM D 814-95 (Reapproved 2000) with the following changes or specifics: The glass jar of ASTM D 814 was replaced with a Thwing-Albert Vapometer

Permeability Cup as described in ASTM E 96-00; the fluoropolymer side of the test specimen was oriented toward the test liquid; the gaskets used were made of Dyneon FE-5840Q elastomer (Shore A hardness of about 60) instead of neoprene rubber and were located on both the top and bottom of the test specimen; a circular disk of mesh screen was used on top of the gasket to prevent the test specimen from deforming during the test; the test liquid was 100 mL of CE 10 fuel (10% ethanol, 45% iso-octane; 45% toluene); and the test temperature was 40°C. The permeation constant ($\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}$) was calculated by measuring the weight loss for a 30-day period using Mettler AT 400 at an accuracy of 0.1 mg. A slope of the line obtained by the least squares fit of weight loss (grams) versus time (days) was divided by the area of the test specimen and multiplied by its thickness.

Example 1

The fluoroelastomer gum, LTFE-1 in the Table 1, and ingredients used in each composition were compounded on a two roll mill using standard methods. Triallylisocyanurate (TAIC) coagent (72% active ingredient, available as TAIC DLC-A from Harwick, Akron, OH), 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane (50% active ingredient, available as Varox DBPH-50 from R.T.Vanderbilt, Norwalk, CT), zinc oxide (available as UPS-1 from Zinc Corporation of America, Monaca, PA), and carbon black (available as Thermax MT, ASTM N990 from Cancarb Limited, Medicine Hat, Alberta, Canada) were combined with the other ingredients.

The compositions of the compounded gums are summarized in Table 2.

The cure rheology of the samples was investigated by testing uncured, compounded mixtures using the Alpha Technology Moving Disk Rheometer (MDR) Model 2000 and the procedure described in ASTM D 5289-95. All samples exhibited good curing properties.

The solvent volume swell was obtained according to ASTM D 471-98 using Fuel K (CM85; 85% methanol, 7.5% iso-octane; 7.5% toluene by volume) at 40°C for 70 hours.

A post cured sheet (press cure: 10 minutes at 177°C, post cure: 16 hours @ 230°C) was cut into a disc having a diameter of 7.72 cm and used for permeation testing. Permeation constants ($\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}$) were obtained according to the above test method using CE 10 fuel (10% ethanol, 45% iso-octane; 45% toluene); and the test temperature was 40°C. The permeation constant results are summarized in Table 2.

Examples 2- 3 and Comparative Example C1 - C2

In Example 2 and 3 and Comparative Examples C1 and C2, the samples were prepared

and tested as in Example 1 except different amounts of carbon black, TAIC coagent and Varox DBPH-50 were added to the fluoroelastomer. The test results are summarized in Table 2.

Example 4

5 In Example 4, the sample was prepared and tested as in Example 1 except the fluoroelastomer gum, LTFE 2 in the Table 1 was used and different amounts of carbon black, TAIC coagent and DBPH-50 were added to the fluoroelastomer. The test results are summarized in Table 2.

Example 5 and Comparative Example C3

10 In Examples 5, the sample was prepared and tested as in Example 4 except different amounts of carbon black, TAIC coagent and DBPH-50 were added to the fluoroelastomer. The test results are summarized in Table 2.

Comparative Example C4

15 In Comparative Example C4, the sample was prepared and tested as in Example 4 except Viton® GLT301 (available DuPont Dow Elastomers, LLC, Wilmington, DE), which does not contain a perfluorinated ether of formula I or formula II as indicated by NMR analysis and has a Tg of -31°C, was used as fluoroelastomer instead of fluoroelastomer LTFE-1 or LTFE-2.
20 Mooney viscosity ML 1 + 10/121°C was 32. The fluoropolymer compound was prepared and tested as in Example 4. The compositions of the compounded gums and properties are summarized in Table 2.

Comparative Example C5

25 In Comparative Example C5, the sample was prepared and tested as in **Comparative Example C5** except different amounts of carbon black. The compositions of the compounded gums and properties are summarized in Table 2.

Table 2

	Ex. 1	Ex. 2	Ex. 3	Co. Ex. C1	Co. Ex. C2	Ex. 4	Ex. 5	Co. Ex. C3	Co. Ex. C4	Co. Ex. C5
LTFE-1	100	100	100	100	100					
LTFE-2						100	100	100		
Viton® GLT305									100	100
N-990	50	55	90	10	30	45	60	30	30	35
ZnO	3	3	3	3	3	3	3	3	3	3
TAIC (72% DLC)	2.08	3.5	1.4	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Varox DBPH-50 (50%Al)	2.5	2.5	2	2.5	2.5	2.5	2.5	2.5	2.5	2.5

MDR at 177°C, 0.5° Arc, 100 cpm, 12 Minutes

ML (dN-m)	3.7	4.5	9.7	3.9	2.9	2.2	2.8	0.6	1.1	1.1
MH (dN-m)	18.4	18.8	30.7	14.4	12.8	17.4	21.2	11.9	19.5	19.2
MH-ML (dN-m)	14.7	14.3	20.9	10.5	9.8	15.2	18.3	11.3	18.4	18.1
TS 2, min	0.4	0.5	0.4	0.54	0.6	0.6	0.5	0.7	0.4	0.4
t'50, min	0.7	0.9	1.0	0.7	0.8	1.0	1.0	1.1	0.6	0.7
t'90, min	2.8	3.1	3.1	1.5	2.3	4.3	4.2	4.5	2.2	2.5

Physical properties

Press Cure Time, 10 min. 177°C,

Tensile (MPa)	11.8	12.1	12.9	9.2	10.7	12.1	11.6	13.6	16	14.3
Elongation (%)	190	167	140	190	218	245	210	311	236	217
100% Modulus (MPa)	7.3	6.5	8.0	2.2	2.7	3.7	4.9	2.3	3.7	5.0
Hardness (Share A2)	70	71	82	55	59	69	74	64	67	67

Post cure Time, 16 h, 230°C

Tensile (MPa)	13.7	12.8	14.2	11.0	13.3	16.1	15.6	14.8	22.9	20.5
Elongation (%)	190	150	120	195	237	200	180	246	213	201
100% Modulus (MPa)	5.4	7.4	14.2	2.3	3.0	5.6	7.1	2.9	5.8	7.2
Hardness (Share A2)	73	75	82	57	61	73	79	63	70	72

Compression Set (%)	26	29	28	15.2	22.4	36	37	29	35	---
---------------------	----	----	----	------	------	----	----	----	----	-----

Fuel K (CM85) volume swell (%) 40°C, 70 hours	10	---	---	---	10	12	10	16	98	---
--	----	-----	-----	-----	----	----	----	----	----	-----

TR-10 (°C)	-39	-39	-39	-40	-40	-31	-31	-31	-30	---
------------	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Permeation constant CE10, 40°C (g-mm/m ² -day)	55	63	50	89	82	49	46	63	68	66
---	----	----	----	----	----	----	----	----	----	----

From the above disclosure of the general principles of the present invention and the preceding detailed description, those skilled in this art will readily comprehend the various modifications to which the present invention is susceptible. Therefore, the scope of the invention should be limited only by the following claims and equivalents thereof.

5

What is claimed is:

1. A compound comprising:
 - (a) an amorphous copolymer including interpolymerized units derived from one or more perfluorinated ethers of the formula:

5 $\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f$ (Formula I) wherein R_f is a perfluorinated (C1 -C4)alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$, or

$\text{CF}_2=\text{CF}(\text{CF}_2)_m-\text{O}-\text{R}_f$ (Formula II) wherein: $m=1-4$; R_f is a perfluorinated aliphatic group optionally containing O atoms; and
 - 10 (b) a curable component including at least one filler having at least 10 parts per 100 parts of component (a), such that upon vulcanization the resulting compound has a Shore A hardness according to ASTM D2240 of 60 or greater, a TR-10 of -25°C or less, and a permeation rate of 65 (g-mm/m²-day) or less.
- 15 2. The compound according to claim 1, wherein said compound includes terpolymers or quadpolymers.
3. The compound according to claim 1, wherein said copolymer includes vinylidene fluoride, tetrafluoroethylene, hexafluoro propylene, vinyl ethers, chloro trifluoro ethylene,

20 pentafluoropropylene, vinyl fluoride, propylene, ethylene or combinations thereof.
4. The compound according to claim 1, wherein said compound is derived from ethylenically unsaturated monomers of the formula $\text{CF}_2=\text{CFR}_f$ where R_f is fluorine or perfluoroalkyl of 1 to 8 carbon atoms.

25
5. The compound according to claim 1, further comprising an effective amount of cure site moieties derived from one or more compounds of the formula: a) $\text{CX}_2=\text{CX}(\text{Z})$, wherein: (i) X is H or F; and (ii) Z is Br, I, Cl or R_fZ U wherein $\text{U}=\text{Br}$, I, Cl, or CN and R_fZ = a perfluorinated divalent linking group optionally containing O atoms; or (b) $\text{Y}(\text{CF}_2)_q\text{Y}$, wherein: (i) Y is Br or

30 I or Cl and (ii) $q=1-6$.
6. The compound according to claim 5, wherein said cure site moieties are derived from $\text{CF}_2=\text{CFBr}$, $\text{CF}_2=\text{CHBr}$, ICF_2 , CF_2 , CF_2 , CF_2 , I , CH_2I_2 , $\text{BrCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFO}(\text{CF}_2)_3-\text{OCF}_2$, CF_2

Br, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{Br}$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{Br}$, $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{I}$, $\text{CF}_2=\text{CFCI}$ or mixtures thereof.

7. The compound according to claim 5, wherein said iodine or said bromine or said chlorine
5 are chemically bound to chain ends of component (a).

8. The compound according to claim 1, wherein said one or more perfluorinated ethers
include $\text{CF}_2=\text{CFOCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$,
10 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2(\text{OCF}_2)_3\text{OCF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2(\text{OCF}_2)_4\text{OCF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$,
15 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{OCF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$,
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{OCF}_3$, or
combinations thereof.

9. The compound according to claim 2, wherein said quadpolymer includes
20 tetrafluoroethylene, vinylidene fluoride, a perfluorinated vinyl ether of the formula
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_3$, and a perfluoromethyl vinyl ether.

10. The compound according to claim 1, wherein said component (a) is formed by emulsion
polymerization.

25 11. The compound according to claim 1, wherein said fillers include carbon black, graphite,
thermoplastic fluoropolymer micropowders, clay, silica, talc, diatomaceous earth, barium
sulfate, wollastonite, calcium carbonate, calcium fluoride, titanium oxide, iron oxide, or
combinations thereof.

30 12. The compound of claim 1, further comprising acid acceptors.

13. The compound of claim 12, wherein said acid acceptors include magnesium oxide, lead oxide, calcium oxide, calcium hydroxide, dibasic lead phosphite, zinc oxide, barium carbonate, strontium hydroxide, calcium carbonate, hydrotalcite, alkali stearates, magnesium oxalate, or combinations thereof.
- 5 14. The compound according to claim 1, wherein said compound has a solvent volume swell in FUEL K (CM85) of about 60% or less, according to ASTM D471-98.
- 10 15. The compound according to claim 1, wherein said curable component is peroxide curable.
16. The compound according to claim 1, wherein said one or more perfluorinated ethers corresponds to formula II and said curable component is a bisphenol curable compound.
- 15 17. A compound comprising:
 (a) a terpolymer including interpolymerized units derived from vinylidene fluoride and one or more perfluorinated ethers of the formula:
 $\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f$ (Formula I) wherein R_f is a perfluorinated (C1 -C4)alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$, or
 $\text{CF}_2=\text{CF}(\text{CF}_2)_m-\text{O}-\text{R}_f$ (Formula II) wherein: $m=1-4$; R_f is a perfluorinated aliphatic group optionally containing O atoms; and
 (b) a curable component including at least one filler having at least 10 parts per 100 parts of component (a), such that upon vulcanization the resulting compound has a Shore A hardness according to ASTM D2240-02 of 60 or greater, a TR-10 of -25°C or less, and a permeation rate of 65 (g-mm/m²-day) or less.
- 20 18. A method of forming an elastomer, comprising vulcanizing a compound having:
 (a) a copolymer including interpolymerized units derived from one or more perfluorinated ethers of the formula:
 $\text{CF}_2=\text{CFO}-(\text{CF}_2)_m-(\text{O}(\text{CF}_2)_p)_n-\text{OR}_f$ (Formula I) wherein R_f is a perfluorinated (C1-C4) alkyl group, $m=1-4$, $n=0-6$, and $p=1-2$, or
- 25 30

$\text{CF}_2=\text{CF}(\text{CF}_2)_m-\text{O}-\text{R}_f$ (Formula II) wherein: $m=1-4$; R_f is a perfluorinated aliphatic group optionally containing O atoms; and

(b) a curable component including at least one filler having at least 10 parts per 100 parts of component (a).

5

19. The method of claim 18, wherein said elastomer has a Shore A hardness according to ASTM D2240-02 of 60 or greater, a TR-10 of -25°C or less, and a permeation rate of 65 (g-mm/m²-day) or less.

10

20. An article comprising a cured compound according to claim 1.

15

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/28472

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F214/18 C08F214/22 C08K3/00 C08K5/14 C08K5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 294 627 B1 (SOKOLOV SERGEY VASILIEVICH ET AL) 25 September 2001 (2001-09-25) cited in the application claims examples; table 3	1-20
X	US 5 696 216 A (KRUEGER RALF ET AL) 9 December 1997 (1997-12-09) example 1	1-20
X	WO 99 48939 A (DYNEON LLC) 30 September 1999 (1999-09-30) page 4, line 14 -page 5, line 9; example 1	1-20
X	US 2001/008922 A1 (ABE KATSUMI ET AL) 19 July 2001 (2001-07-19) examples 1,2	1-20
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

26 January 2004

Date of mailing of the international search report

02/02/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Baekelmans, D

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/28472

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 308 467 A (SOLVAY SOLEXIS S P A) 7 May 2003 (2003-05-07) claims 1-3,16; examples; table 1 -----	1-20
A	US 2001/000343 A1 (BOWERS STEPHEN) 19 April 2001 (2001-04-19) page 2, paragraphs 27-30; claims page 5, paragraph 63 -----	1-20
A	WO 02 44263 A (DUPONT DOW ELASTOMERS LLC) 6 June 2002 (2002-06-06) page 5, line 15 -page 6, line 5 page 14, line 14 - line 26 -----	1-20

Form PCT/ISA/210 (continuation of second sheet) (July 1982)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/28472

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6294627	B1	25-09-2001	CA 2341460 A1 CN 1321170 T DE 69913550 D1 EP 1117710 A1 JP 2002523576 T WO 0012574 A1	09-03-2000 07-11-2001 22-01-2004 25-07-2001 30-07-2002 09-03-2000
US 5696216	A	09-12-1997	DE 19542501 A1 CN 1152583 A , B DE 59601258 D1 EP 0774472 A1 JP 9286824 A	22-05-1997 25-06-1997 18-03-1999 21-05-1997 04-11-1997
WO 9948939	A	30-09-1999	BR 9908975 A CA 2324954 A1 CN 1294601 T EP 1068248 A1 JP 2002507640 T WO 9948939 A1	05-12-2000 30-09-1999 09-05-2001 17-01-2001 12-03-2002 30-09-1999
US 2001008922	A1	19-07-2001	JP 2001181350 A DE 10063993 A1	03-07-2001 28-06-2001
EP 1308467	A	07-05-2003	IT MI20012165 A1 EP 1308467 A2 JP 2003137930 A US 2003119993 A1	18-04-2003 07-05-2003 14-05-2003 26-06-2003
US 2001000343	A1	19-04-2001	US 6329469 B1 US 2002035220 A1 EP 1109844 A1 JP 2003525308 T WO 0011050 A1	11-12-2001 21-03-2002 27-06-2001 26-08-2003 02-03-2000
WO 0244263	A	06-06-2002	WO 0244263 A1 EP 1337583 A1	06-06-2002 27-08-2003